Experimental Evidence for Kaplan–Shekhtman–Entin-Wohlman–Aharony Interactions in $Ba_2CuGe_2O_7$

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New neutron diffraction and inelastic neutron scattering experiments on $Ba_2CuGe_2O_7$ suggest that the previously suggested model for the magnetism of this material (an ideal sinusoidal spin spiral, stabilized by isotropic exchange and Dzyaloshinskii-Moriya interactions) needs to be refined. Both new and previously published experimental results can be quantitatively explained by taking into account the Kaplan-Shekhtman-Entin-Wohlman-Aharony term, a special anisotropy term that was predicted to always accompany Dzyaloshinskii-Moriya interactions in insulators. [S0031-9007(98)07926-5]

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Among the more exotic magnetic interactions in solids is the so-called asymmetric exchange, first predicted theoretically by Dzyaloshinskii [1]. Unlike conventional Heisenberg exchange coupling that is proportional to the *scalar* product $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ of interacting spins, asymmetric exchange is proportional to the corresponding *vector* product. In the spin Hamiltonian it is usually written as $\boldsymbol{D}(\boldsymbol{S}_1 \times \boldsymbol{S}_2)$, where $\boldsymbol{D}$ is the Dzyaloshinskii vector associated with the bond between the two interacting magnetic ions. A microscopic model for asymmentric exchange interactions was first proposed by Moriya [2], and is essentially an extension of the Anderson superexchange mechanism [3] that allows for spin-flip hopping of electrons. While forbidden by symmetry in centrosymmetric crystal structures, Dzyaloshinskii-Moriya (DM) interactions were found to be active in a number of noncentric compounds, where they lead to either a weak ferromagnetic or helimagnetic distortion of the collinear magnetic state [4–6]. The inclusion of the DM term breaks the $O(3)$ invariance of the originally isotropic Heisenberg spin Hamiltonian, reducing the symmetry to $O(2)$: To take full advantage of the cross product term the interacting spins must be perpendicular to the vector $\boldsymbol{D}$. Dzyalashinskii-Moriya interactions thus play the role of an effective two-ion easy-plane anisotropy, with the easy plane normal to the vector $\boldsymbol{D}$.

Only relatively recently have Kaplan [7] and, independently, Schekhtman, Entin-Wohlman, and Aharony [8,9] realized that there is *more* to Moriya's mechanism than just the vector-product term. For very fundamental reasons the DM cross product must always be accompanied by a two-ion easy-axis anisotropy term that exactly compensates the easy-plane effect of the vector product. The additional Kaplan–Shekhtman–Entin-Wohlman–Aharony (KSEA) term can to a good approximation be written as $\frac{1}{2J}(\boldsymbol{S}_1\boldsymbol{D})(\boldsymbol{S}_2\boldsymbol{D})$, where J is the Heisenberg (isotropic) component of superexchange coupling. Often referred to as "hidden symmetry," the KSEA term *restores* the O(3) invariance of the Hamiltonian, at least locally. Originally, the KSEA term was invoked to explain the spin anisotropy in the orthorhombic phase of La_2CuO_4 [8–10]. It was later realized that this term alone cannot account for all of the observed effects, particularly for the magnetic anisotropy seen in the tetragonal phase [11–13]. To our knowledge, to date there has been no "clean" experimental evidence unambiguously pointing to the presence of KSEA interactions. In the present paper we present such experimental data for the helimagnetic insulator $Ba_2CuGe_2O_7$. We demonstrate that only by taking into account the KSEA term can one obtain qualitatively and quantitatively correct predictions for the magnetic structure and spin wave spectrum.

As was shown in a series of recent publications [14–17], $Ba_2CuGe_2O_7$ is a particularly useful model system for studying DM interactions. The magnetism of this compound is due to Cu^{2+} ions that form a square lattice in the (a,b) tetragonal plane of the crystal. The principal axes of this square lattice, hereafter referred to as the x and y axes, run along the $[110]$ and $[1\bar{1}0]$ crystallographic directions, respectively. To complete the coordinate system we choose the z axis along the $[001]$ direction. In the magnetically ordered phase (below $T_N = 3.2$ K) all spins lie in the $(1\bar{1}0)$ plane (see inset of Fig. 1). The magnetic propagation vector is $(1+\zeta,\zeta,0)$, where $\zeta = 0.0273$, and $(1,0,0)$ is the antiferromagnetic zone center. The magnetic structure is a distortion of a Néel spin arrangement: A translation along $(\frac{1}{2},\frac{1}{2},0)$ induces a spin rotation by an angle $\phi = 2\pi\zeta \approx 9.8°$ (relative to an exact antiparallel alignment) in the $(1,\bar{1},0)$ plane. Along the $[1\bar{1}0]$ direction, nearest-neighbor spins

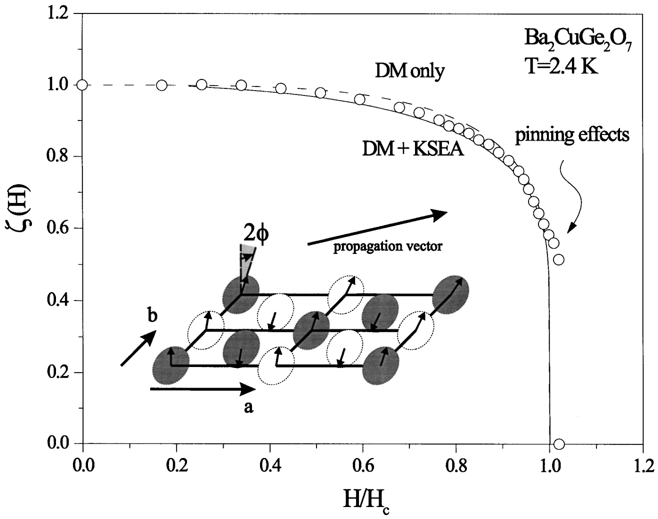

FIG. 1. Field dependence of the incommensurability parameter ζ, as previously measured in $Ba_2CuGe_2O_7$ (Refs. [16,17]). The solid and dashed lines are theoretical predictions that do (this paper) or do not (Ref. [16]) take into account the KSEA interactions, respectively. Inset: A schematic of the spiral spin arrangement in $Ba_2CuGe_2O_7$.

are perfectly antiparallel. Spins in adjacent Cu planes are aligned parallel to each other. Only nearest-neighbor in-plane isotropic superexchange antiferromagnetic interactions are important ($J \approx 0.96$ meV, as determined by the measured spin wave bandwidth [14]). The helical state is stabilized by DM interactions. In the current model Dzyaloshinskii vectors for nearest-neighbor Cu-Cu pairs lie in the (x, y) plane and are oriented perpendicular to their corresponding bonds: $\boldsymbol{D} \parallel y$ for an x bond and $\boldsymbol{D} \parallel x$ for y bonds, respectively (Fig. 1 in Ref. [16]). The corresponding energy scale is $D \approx 0.17$ meV. In the discussion below we shall use the numerical values for J and ζ quoted above as given, and perform all calculations without using any adjustable parameters.

In $Ba_2CuGe_2O_7$, KSEA easy axes that correspond to the y Cu-Cu bonds are parallel to the x axis, i.e., lie *in the plane of spin rotation*. Regions of the slowly rotating spin spiral where the local staggered magnetization $\boldsymbol{l}$ is almost parallel to x become more energetically favorable than those where $\boldsymbol{l}$ is almost parallel to z (crystallographic c axis). The KSEA anisotropy must therefore lead to a distortion of the ideal sinusoidal spiral, and modify the period of the structure. The KSEA term is expected to produce exactly the same distortion as a magnetic field H applied along the z axis: The latter also has the effect of forcing the local staggered magnetization into the (x, y) plane. The role of a z-axis field is rather dramatic and has been studied in detail [16,17]. The period of the spiral increases with increasing H and diverges at $H_c \approx 2.15$ T, resulting in a commensurate spin-flop antiferromagnetic state at $H > H_c$. For $0 < H < H_c$ the spin structure is described as a "soliton lattice," where regions of the commensurate phase are interrupted by regularly spaced antiferromagnetic domain walls. In the soliton phase, in addition to the principal magnetic Bragg peaks at $(1 \pm \zeta, \pm\zeta, 0)$, characteristic of an ideal spiral, one expects to see all odd magnetic Bragg harmonics at $(1 \pm 3\zeta, \pm 3\zeta, 0)$, $(1 \pm 5\zeta, \pm 5\zeta, 0)$, etc. By comparing the experimental field dependencies of ζ and the higher-order Bragg peaks to theoretical predictions for the "DM-only" (Refs. [16,17]) and "DM + KSEA" models, we can hope to obtain direct evidence for KSEA interactions in $Ba_2CuGe_2O_7$.

We can make the above discussion quantitative by including the KSEA term into the phenomenological energy functional that was previously used to describe the behavior of $Ba_2CuGe_2O_7$ in the framework of the DM-only model [16,17]. This procedure is rather straightforward and the principal conclusion is that all previously obtained DM-only results can be recycled, by replacing H in all equations by the *effective* field

$$H^{\mathrm{eff}} = \sqrt{H^2 + 2A\rho_S/(\chi_\perp - \chi_\parallel)}\,. \tag{1}$$

Here $\rho_S \approx JS^2$ is the spin stiffness, $\chi_\perp$ and $\chi_\parallel$ are the local transverse and logitudinal susceptibilities, respectively, and the KSEA term is represented by $A = \alpha^2/2 \approx D^2/2J^2$. The parameter α is defined by $\tan\alpha \equiv D/J$, and is equal to the spin rotation angle ϕ in the DM-only model. According to our continuous-limit calculations, in the DM + KSEA model $\alpha \equiv \arctan(D/J) \cong \frac{32}{31}\phi$.

Let us consider the field dependence of the incommensurability parameter ζ that, for the DM + KSEA model can be obtained by replacing H by H^{eff} in Eqs. (4) and (7) in Ref. [16]. In Fig. 1 we replot the $\zeta(H)$ data from Ref. [16] in reduced coordinates. The solid and dashed lines are the theoretical curves plotted with and without taking into account the KSEA interactions, respectively. We see that the inclusion of the KSEA term hardly affects the *shape* of the $\zeta(H)$ curve. However, the theoretical prediction for H_c is substantially different in the DM-only and DM + KSEA models. Combining Eq. (1) from above with Eq. (5) in Ref. [16], one readily obtains

$$H_c = \alpha\,\frac{\sqrt{\pi^2 - 4}}{2}\sqrt{\frac{\rho_s}{\chi_\perp - \chi_\parallel}}\,, \tag{2}$$

For the low-temperature limit in $Ba_2CuGe_2O_7$ we can use the classical expressions $\rho_s = JS^2 = 0.24$ meV, $\chi_\parallel = 0$, and $\chi_\perp = (g_c\mu_B)^2/8J$, where $g_c = 2.47$ is the c-axis gyromagnetic ratio for Cu^{2+} in $Ba_2CuGe_2O_7$ [18]. Substituting $\alpha = 2\pi\frac{32}{31}\zeta = 0.177$, we get the estimate for the critical field $H_c = 2.05$ T. This value is much closer to the experimental value $H_c \approx 2.15$ T than our previous estimate $H_c \approx 2.6$ T [19], obtained without taking into account the KSEA term.

As mentioned, KSEA interactions have a substantial influence on the intensity of higher-order Bragg harmonics. In the DM-only model in zero field, the higher-order Bragg reflections are totally absent. For the DM + KSEA model, combining our expression for H^{eff} with Eqs. (17) and (18) in Ref. [17], for the relative intensities of the first and third harmonics, in the small field limit (weakly distorted spiral) $|\phi - \alpha| \ll \phi$ we get

$$\frac{I_3}{I_1} = \left[\frac{1}{16} + \left(\frac{\pi^2}{64} - \frac{1}{16} \right) \left(\frac{H}{H_c} \right)^2 \right]^2 . \qquad (3)$$

In zero field this gives $I_3/I_1 = 1/256 \approx 4 \times 10^{-3}$.

To verify the relation (3) we performed new magnetic neutron scattering experiments on $Ba_2CuGe_2O_7$ single crystal samples. The measurements were done in two experimental runs, on the IN-14 3-axis spectrometer at the Institut Laue Langevein (ILL) in Grenoble, and the SPINS spectrometer at the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST). The samples were similar to those used in previous studies [17]. In each experiment the crystals were mounted with their c axes vertical, making $(h, k, 0)$ wave vectors accessible for measurements. The data were collected at temperatures in the range 0.35–5 K. Neutrons of energies 3.5 or 2.5 meV were used in most cases. In Figs. 2(a) and 2(b) we show some typical elastic scans along the $(1 + \epsilon, \epsilon, 0)$ reciprocal-space line measured in $Ba_2CuGe_2O_7$ at low temperatures in zero and $H = 1$ T applied fields. Even in the zero-field data, in addition to the first-order principal magnetic reflection, one clearly sees the third order harmonic. The measured field dependence of I_3/I_1 (ratio of Q-integrated intensities) is shown in Fig. 2(c). In our measurements we have taken special care to verify that the relative intensities of the two peaks are totally independent of the $T - H$ history of the sample (zero-field cooling vs. cooling in a 3 T magnetic field). The solid and dashed lines in Fig. 2(c) represent the predictions of the DM + KSEA [Eq. (3)] and DM-only (Ref. [16,17]) models, respectively. For these theoretical curves we used the experimental numerical values, and no adjustable parameters. An almost perfect agreement between the DM + KSEA model and the experimental data is apparent, and so is the failure of the DM-only model.

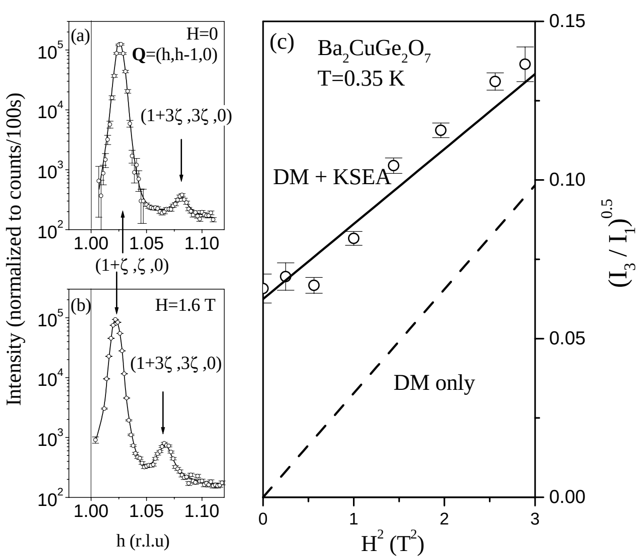

FIG. 2. Typical elastic scans along the $(1, 1, 0)$ direction in the vicinity of the antiferromagnetic zone-center $(1, 0, 0)$, measured in $Ba_2CuGe_2O_7$ at $T = 0.35$ K in zero field (a) and in a $H = 1.6$ T magnetic field (b) applied along the c axis. (c) The square root of the measured ratio of the intensities of the $(1 + 3\zeta, 3\zeta, 0)$ and $(1 + \zeta, \zeta, 0)$ peaks plotted against the square of the applied field. The lines are guides for the eye in (a) and (b) and theoretical curves in (c), as in Fig. 1.

It is clear that the KSEA anisotropy term will also affect the spin wave spectrum. For an ideal spin spiral (DM-only model) the classical spin wave dispersion relations can easily be obtained analytically by using the Holstein-Primakov formalism, as shown in Fig. 3(a) for $Ba_2CuGe_2O_7$. Two acoustic branches (hereafter referred to as the $\pm\zeta$ modes) emerge from the two magnetic Bragg peaks at $(1 \pm \zeta, \zeta, 0)$. A third branch (the 0 mode) has a gap at the antiferromagnetic zone center, equal to D. This branch almost exactly passes through the intersection point of the $\pm\zeta$ modes. The actual dispersion curves in $Ba_2CuGe_2O_7$ were measured in constant-Q inelastic scans using the experimental setups described above in the fixed-incident-energy mode. Incoherent scattering and Bragg "tails" prevented us from collecting reliable data for energy transfers of less than $\approx$0.17 meV. A typical inelastic scan (raw data) is shown in Fig. 4. Combined data from the two series of experiments are summarized in the experimental dispersion relations in Fig. 3(b) (symbols). The two $\pm\zeta$ modes do not intersect at the Néel point. Instead, at $\mathbf{Q} = (1, 0, 0)$ there is a clear repulsion between these two branches. This repulsion is again manifest at $\mathbf{Q} = (1 + 2\zeta, 2\zeta, 0)$ and is seen as a discontinuity in the $+\zeta$ branch. We also note that the 0 mode lies visibly lower than the extrapolated point of intersection of the $\pm\zeta$ branches (dashed lines). Obviously, the DM-only model fails to reproduce the observed dispersion relations. The spin wave spectrum in the presence

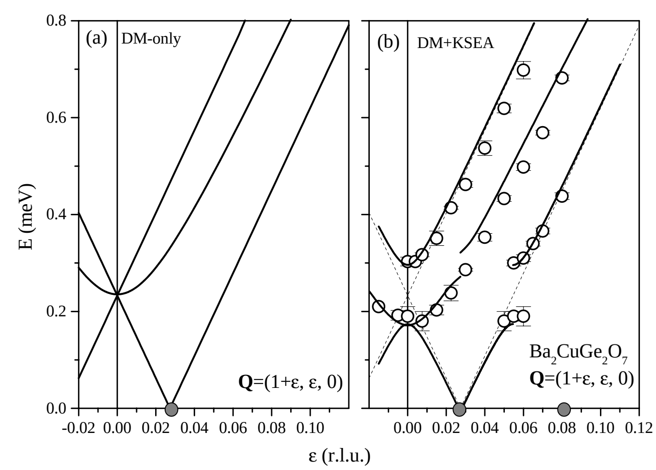

FIG. 3. (a) Classical spin wave dispersion relations calculated for $Ba_2CuGe_2O_7$ without taking into account the KSEA interactions. (b) Solid lines: same as (a), with the SEA term included. Symbols: experimental dispersion curves measured in $Ba_2CuGe_2O_7$ at $T = 0.35$ K and $T = 1.5$ K with inelastic neutron scattering.

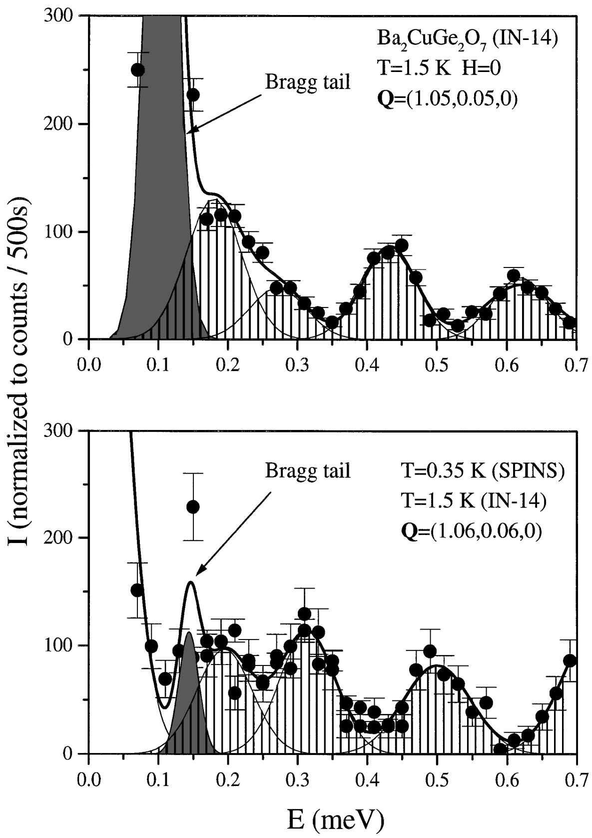

FIG. 4. Typical inelastic scans measured in $Ba_2CuGe_2O_7$ at $T = 1.5$ K and $T = 3$ K (combined data in lower plot). The shaded curves represent the individual Gaussians in a multipeak fit (heavy solid line). The solid gray area shows the position of a "Bragg-tail" spurious peak.

of KSEA interactions can be derived in the limit $|\phi - \alpha| \ll \phi$, a condition well satisfied in $Ba_2CuGe_2O_7$, using the series expansion method described in Refs. [20,21]. Performing this somewhat tedious calculation for $Ba_2CuGe_2O_7$, we obtain the dispersion relations shown in solid lines in Fig. 3(b), and find very good agreement with experiment with *no adjustable parameters*.

In summary, both the static and dynamic magnetic properties of $Ba_2CuGe_2O_7$ are *quantitatively* consistent with the presence of KSEA interactions. It is important to stress that in a *slowly* rotating spiral the KSEA term (a pair of easy axes) is impossible to distinguish from any conventional easy-plane anisotropy terms. In our case these effects are too small to be studied experimentally. Another player in the Hamiltonian that could affect the distortion of the spin spiral is the dipolar term. Its energy scale is given by $(g\mu_B)^2/a^3$, which in $Ba_2CuGe_2O_7$ is over an order of magnitude smaller than the frustration $D^2/2J$ caused by the KSEA term. Moreover, dipolar interactions are strongly suppressed in an *antiferromagnetic* structure due to their long-range sign-alternating nature. In any case, the issue that we tried to address above is not whether or not KSEA interactions *exist*: If one believes Anderson's and Moriya's superexchange mechanisms, one is forced to accept the presence of the KSEA term as well. Rather, we have demonstrated that KSEA interactions can result in very interesting effects, and that no *additional* anisotropy is needed to reproduce the behavior observed in $Ba_2CuGe_2O_7$.

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